Synthesis, Characterization, and Reactivity of Palladium(II) Salen and Oxazoline Complexes

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Two methods for the syntheses of palladium(II) salen complexes are described. The first involves template synthesis of the ligand in which bis(salicylaldehydato)palladium(II), **2**, is initially synthesized and reacted with the appropriate diamine bridge to yield the desired palladium salen. The template synthesis approach suffers, however, from low overall yields (17−30%). Alternatively, treatment of bis(acetonitrile)palladium(II) chloride with the appropriate salen ligand under inert atmosphere yields the palladium salen complex in high yields (80−85%). [2-(2′-Hydroxyphenyl)-2-oxazolinato]palladium(II), **7**, was also synthesized. All the palladium complexes were fully characterized spectroscopically. A single-crystal X-ray structure of **7** has been solved. In contrast to previous reports, complex **2** was found to be stable over weeks and remained suitable for the template syntheses. The catalytic activity of complex **2** in cyclopropanation of alkenes with ethyl diazoacetate (EDA) was investigated. The catalyst is not functional group tolerant and works best for styrene; turnover numbers (TON's) of 45 were achieved. The availability of an open coordination site seems to be a prerequisite for catalytic decomposition of EDA.

Introduction

Transition-metal salen and oxazoline complexes have been successfully employed in a number of catalytic reactions, including olefin epoxidation,[1−5] aziridination,[6] cyclopropanation,[7−11] oxidation of sulfides,[12] oxidation of hydrocarbons,[13] and hetero-Diels−Alder reactions,[6,14] to name a few. The introduction of chiral auxiliaries on salen and oxazoline ligands has revived and extended their catalytic chemistry to include asymmetric transformations. Worthy of mention is the work of Jacobsen[15,16] and Katsuki[17,18] employing chiral manganese(III) salen derivatives with hypochlorite for enantioselective preparation of unfunctionalized epoxides.

Even though salen and oxazoline complexes of first-row transition elements are widely employed and easily prepared, complexes of second-row d metals are less common, particularly those of rhodium[19−21] and palladium.[22] Palladium(II) complexes with bidentate Schiff-base ligands have been reported as catalysts for the hydrogenation of aromatic nitro compounds with dihydrogen under ambient conditions;[23] also, dimeric Pd(II) Schiff-base complexes were found to exhibit second-order NLO properties.[24] Thus, in view of the general utility of palladium in catalysis, we have undertaken the task of preparing palladium salen and oxazoline complexes and exploring their reactivities. We report herein two pathways for the synthesis of palladium salen derivatives. Full spectroscopic characterizations of all compounds are reported along with a single-crystal X-ray structure of [2-(2′-hydroxyphenyl)-2-oxazolinato]palladium(II), **7**. In addition, experiment and theory are applied to clarify earlier findings regarding the stability of bis(salicylaldehydato)palladium(II), **2**. Finally, we describe the catalytic reactivity of these palladium complexes in cyclopropanation of alkenes with ethyl diazoacetate.

Results and Discussion

Synthesis and Spectroscopic Characterization of Palladium(II) Salen Complexes. The palladium salen-derivative complexes were prepared by two routes which are depicted in Scheme 1. The template synthesis of the ligand, method A, was initially employed by Patel in the preparation of palladium(II)

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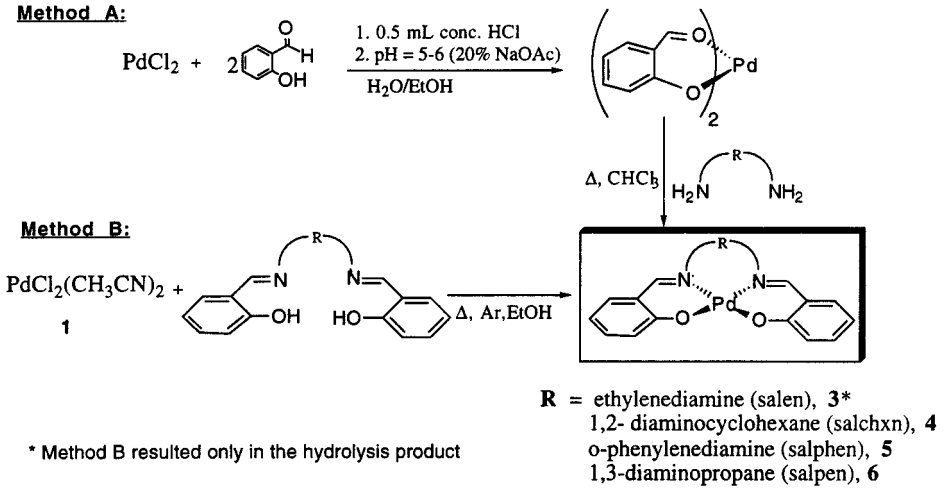
Scheme 1. Synthetic Pathways for Palladium(II) Salen Complexes



salen complexes with alkyl substituents on the ethylenediamine bridge.[22] This approach is time consuming because it requires the isolation and recrystallization of the bis(salicylaldehydato)-palladium(II), **2**, followed by condensation with the diamine bridge. The low overall yields obtained from method A were mainly due to the low yields in making **2**. An advantage of method A, however, is the convenience of running the reactions without exclusion of air or moisture. In contrast, method B, which involves the reaction of the free ligand with $PdCl_2(CH_3CN)_2$, **1**, must be carried out in dry solvent and under inert atmosphere. Method B provides higher yields (81−85% yields) than method A (17−30% overall yields). Nevertheless, we were unable to prepare the parent Pd(II) salen complex, **3**, via method B. All attempts resulted in only the isolation of the hydrolysis product, **2**.

The ^{1}H NMR spectra of all the metal complexes support successful chelation of the ligand in a square planar geometry. The proton of the imine carbon in the palladium complexes is shifted 0.1−0.8 ppm downfield relative to the ligand; also the −OH signal of the free ligand (∼12 ppm) is absent from the spectra of palladium complexes, indicating deprotonation of the phenoxide oxygens and their coordination to the metal. The characteristic C═N stretch (1342−1266 cm^{-1}) of the ligands is shifted by 80−150 cm^{-1} to lower wavenumbers for the palladium complexes, which is also indicative of bond weakening due to coordination. In addition, cationic FAB mass spectrometry successfully confirmed the reported palladium complexes and displayed M^+ with the correct isotope pattern for palladium as the major species. The exact compositions of the complexes were verified by elemental analyses.

Preparation of [2-(2′-Hydroxyphenyl)-2-oxazolinato]palladium(II), 7, and Its X-ray Molecular Structure. **7** was prepared directly from **1** and the oxazoline ligand in methylene chloride under inert atmosphere analogous to method B. The crude product was recrystallized from CH_2Cl_2 to give yellow crystals. The single-crystal X-ray structure of **7** contains isolated molecules with square planar geometry around the palladium, Figure 1. Two half-molecules with virtually identical parameters constitute the asymmetric unit. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The preferred stereochemical arrangement has the phenoxide oxygens trans to each other, which is consistent with other Schiff-base complexes of palladium that have been structurally characterized.[25] The Pd−O distance of 1.982 Å and Pd−N distance of 1.983 Å are in the range observed for other palladium complexes.[26,27] Complete crystallographic tables containing (1) positional and equivalent isotropic thermal parameters, (2) anisotropic thermal parameters, (3) bond lengths, and (4) bond angles are included in the Supporting Information.

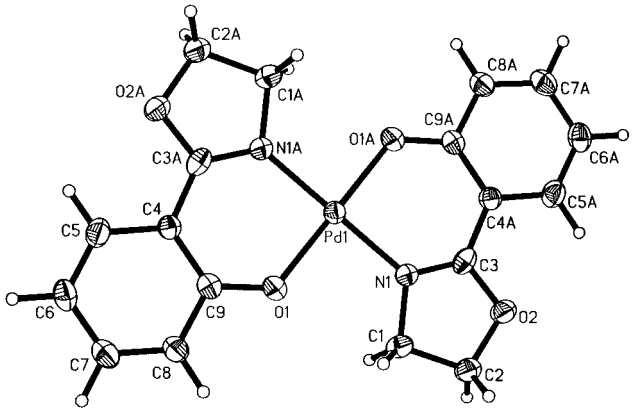
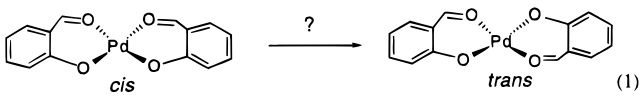


Figure 1. ORTEP drawing of the molecular structure of [2-(2-hydroxyphenyl)-2-oxazolinato]palladium(II), **7**.

Stability and Stereochemistry of 2 and Their Relevance to Synthesis. Earlier reports have claimed that bis(salicylaldehydato)palladium(II), **2**, decomposes rapidly to a black solid.[22,28] Thus in our earlier syntheses via method A (Scheme 1), **2** was prepared and promptly employed in making complexes **3**−**6**. However, aging samples of **2** in our hands showed no signs of disintegration; over periods of weeks, neither the UV−vis nor the ^{1}H NMR spectrum of **2** displayed any changes. We initially speculated that perhaps **2** isomerizes from *cis* to *trans* slowly, eq 1, and that the *trans* isomer is not fit for the ligand template synthesis.



(1)

To investigate further the hypothesis that two stereoisomers of **2** may be present in solution, we carried out a 2D ^{1}H NMR

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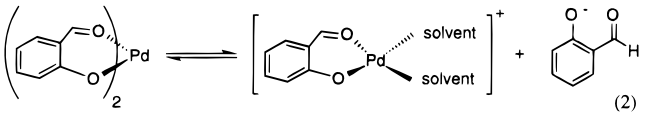
Table 1. Details of the X-ray Data Collection and Structure Refinement for Complex **7**

empirical formula	$C_{18}H_{16}N_2O_4Pd$
fw	430.73
temp	295(2) K
radiation; λ	Mo Kα; 0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
cryst color	yellow
cryst habit	needle
unit cell dimens	$a = 10.277(7)$ Å, $b = 12.164(9)$ Å, $c = 7.058(5)$ Å, $\alpha = 95.37(4)°$, $\beta = 98.65(3)°$, $\gamma = 108.27(3)°$
Z	2
V	818.9(10) Å^3
ρ(calcd)	1.747 Mg/m^3
abs coeff (μ)	1.159 mm^{-1}
F(000)	432
cryst size	0.35 × 0.10 × 0.10 mm
diffractometer	Picker (Crystal Logic)
2θ range, deg	2.13−27.49
reflns collected	3104
no. of indep reflns	3104 [R(int) = 0.0000]
abs cor	semiempirical
max and min transmn	1.00 and 0.587
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3104/0/229
final R indices [$I > 2\sigma(I)$]	R1 = 0.0337, wR2 = 0.0796
R indices (all data)	R1 = 0.0698, wR2 = 0.0974
GOF = $(\sum w(\|F_o\| - \|F_c\|)^2/(N_o - N_v))^{1/2}$	1.003

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **7**

Pd(1)−O(1)	1.982(4)	O(1)−Pd(1)−N(1)	88.9(2)
Pd(1)−N(1)	1.983(4)	C(3)−N(1)−Pd(1)	126.8(4)
O(2)−C(3)	1.348(6)	N(1)−C(3)−C(4)	127.0(5)
N(1)−C(3)	1.284(6)	C(3)−C(4)−C(9)	121.9(5)
0(1)−C(9)	1.308(6)	C(9)−O(1)−Pd(1)	127.4(3)

(NOESY) experiment with complex **2** in DMSO. The 2D NMR spectrum, Figure S1 (Supporting Information), displays dynamic behavior in which free and coordinated salicylaldehydes are rapidly exchanging. Consequently, we performed variable-temperature NMR experiments on complex **2** in different solvents ($CDCl_3$ and DMSO-d_6). The ^{1}H NMR spectrum of **2** in coordinating solvents exhibits two peaks at 8.58 and 8.49 ppm in the ratio of 2:1 that are due to bis- and mono-(salicylaldehydato)palladium(II) complexes, respectively, eq 2.



(2)

On the other hand, in noncoordinating solvents such as CD_2Cl_2, the ratio of the peaks at 8.23 and 8.31 ppm is 4.5:1. ^{1}H NMR spectra were acquired in $CDCl_3$ from 218 to 330 K, and in DMSO-d_6 from 300 to 400 K. No significant changes in the ^{1}H spectra were seen as a function of temperature besides that at high temperature (≥380 K) the amount of free salicylaldehyde increases. Furthermore, density functional theory (DFT) calculations using B3LYP/g-31*/Hay−Wadt(ECP) or B3LYP/LanL2DZ show that both stereoisomers of **2**, *cis* and *trans*, are comparable in energy, Figure S2 (Supporting Information).

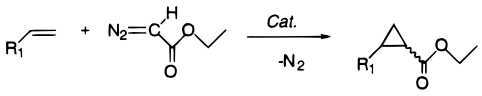
In view of these findings, we anticipated that aged samples of complex **2** should still be fit for synthesizing palladium salen complexes. Thus we synthesized a batch of **2** and divided it into three equal portion, which were used with 1,2-*trans*-diaminocyclohexane to make complex **4** at different times: (1) the same day **2** was prepared, (2) 3 days later, and (3) 2 weeks later. The isolated yields of **4** from the three syntheses were 70, 69, and 75%, respectively. In other words, the isolated yields of **4** were the same within experimental reproducibility regardless how old complex **2** was. Therefore, we contend that the solvent exchange of **2** is rapid on the time scale of the syntheses and that **2** is a stable compound over weeks in contrast to earlier claims of rapid decomposition to palladium metal.[22,28]

Table 3. Cyclopropanation of Alkenes with EDA Catalyzed by Complex **2**[a]

entry	alkene (EDA:alkene)	% catalyst[b]	% yield[c] of cyclopropyl ester (trans:cis)[d]
1	styrene (2)	1	45 (1.6)
2	styrene (5)	1	48 (1.5)
3	styrene (2)	5	54 (1.6)
4	styrene (2) in CH_3CN	1	5
5	α-methylstyrene (2)	1	4
6	*trans*-β-methylstyrene (2)	1	6
7	cinnamyl alcohol (2)	1	4
8	(trimethylsiloxy)ethylene (2)	1	8
9	methyl vinyl ketone (2)	1	0
10	1-heptene (2)	1	0

[a] In $CDCl_3$ at room temperature unless specified otherwise. [b] Relative to olefin. [c] Calculated by NMR based on starting olefin. The products from EDA were either cyclopropane (from reaction with alkene) or maleate and fumurate (from coupling of EDA): fumurate:maleate = 1.5:2.0 determined by NMR. [d] Trans:cis determined by J values from NMR and by GC.

Catalytic Activity of 2 in Cyclopropanation of Alkenes with EDA. Complex **2** catalyzes carbene transfer from ethyl diazoacetate (EDA) to several alkenes, eq 3. The results from



(3)

several runs with different olefins are summarized in Table 3. The catalytic reactions exhibit no significant stereoselectivity in the cyclopropyl ester product, which is expected for most catalysts that lack bulky ligands,[29] rhodium and iron porphyrin catalysts being the exceptions.[30,31] The best yields for the cyclopropyl ester from styrene were obtained when EDA was used in excess of alkene. To enhance selectivity (i.e., cyclopropane versus coupling products), EDA was added slowly via a pump syringe to a solution of alkene and catalyst. Since the yields reported in Table 3 are based on olefin, they also reflect the selectivity toward the cyclopropyl product. The remaining balance of EDA is always converted to coupling products, maleate and fumurate.

The substrate selectivity of catalyst **2** is difficult to rationalize, but it is clear that this catalyst does not tolerate functionality. For example, cinnamyl alcohol (entry 7, Table 3) and (trimethylsiloxy)ethylene, a silyl enol ether (entry 8), give very poor yields. In addition, 1-heptene (entry 10) and methyl vinyl ketone (entry 9) give no detectable cyclopropyl ester. Disubstituted arylalkenes (entries 5 and 6) result in much poorer yields in comparison to styrene (entry 1), a monosubstituted olefin. Analogous bias toward substrate was observed for iron(II) porphyrin catalysts.[31] Changing the solvent clearly affects the yields (entry 4) but has very little or no effect on the stereoselectivity.

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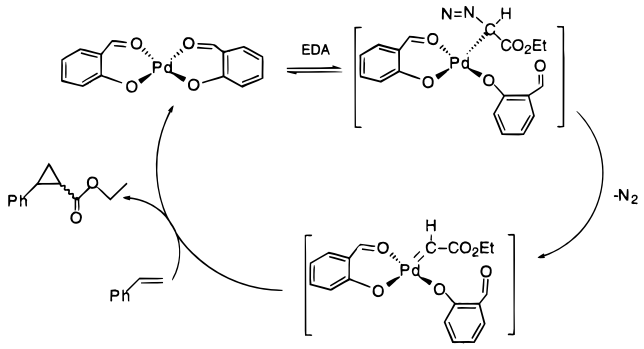
Scheme 2. Catalytic Cyclopropanation of Styrene with EDA Catalyzed by **2**



Palladium salen complexes **3**−**6** did not affect the decomposition of EDA (results not shown). Reasoning that perhaps a catalyst that is structurally similar to **2** is necessary for catalysis, we synthesized the bis(oxazolinato)palladium complex **7**. Nevertheless, when **7** was screened as a catalyst for EDA decomposition, it exhibited very low activity. In the presence of 0.5 mol % of **7** and 2.0 mmol of EDA, only 5% yield of coupling products, maleate and fumurate, was formed after 20 h. Therefore, **7** is not a viable catalyst for the cyclopropanation reaction. It is worth noting that, unlike **2**, complex **7** does not exhibit facile ligand exchange (*vide supra*). These findings indicate that the square planar Pd(II) must have a good leaving group that provides an open coordination site for EDA binding prior to the formation of a palladium carbene intermediate. Recently, Denmark and co-workers illustrated such a requirement in palladium(II)-catalyzed cyclopropanations with diazomethane.[11] Hence, complex **2** is an effective catalyst because it exhibits rapid ligand exchange in solution (*vide supra*), allowing initial coordination of EDA and subsequent formation of a palladium carbene intermediate, Scheme 2.

Due to our interest in the mechanistic chemistry of metal-mediated carbenoid transfer, we followed the reaction of **2** with EDA by NMR at low temperatures. A stoichiometric amount of EDA was added to a solution of **2** (5.0×10^{-3} M) in $CDCl_3$ at 218 K. ^{1}H NMR spectra were acquired at 10-deg intervals from 218 to 308 K. No intermediates were observed. The spectra until room temperature (300 K) were that of EDA and complex **2**; at room temperature after 2 h, the reaction was complete with maleate and fumurate as the only products. Throughout the reaction, no appreciable amounts of an intermediate were accumulated to allow its detection.

Conclusions. Several palladium(II) salen complexes were synthesized successfully by two different methods. One synthetic route involves ligand template synthesis starting with the bis(salicylaldehydato)palladium(II) and the desired diamine. An alternative route employs a single-step synthesis in which bis(acetonitrile)palladium(II) chloride is combined with the salen ligand in dry solvent under inert atmosphere. The direct one-step synthesis afforded higher yields as compared to the ligand template pathway. However, the synthesis of the parent palladium salen complex, **3**, was unsuccessful via the direct route; only hydrolysis products were recovered. In addition, [2-(2′-hydroxyphenyl)-2-oxazolinato]palladium(II), **7**, was synthesized and its X-ray molecular structure was solved. When investigated as potential catalysts for the cyclopropanation of alkenes with EDA, the palladium(II) salen complexes and **7** were found ineffective. However, the bis(salicylaldehydato)palladium(II) precursor was a viable catalyst for the cyclopropanation of styrene.

Experimental Section

Materials and Instrumentation. The diamines and salicylaldehyde were obtained from Acros Organics Chemical Co., Fisher Chemicals, and Aldrich Chemical Co. Palladium chloride and bis(acetonitrile)-dichloropalladium(II) were donated by Alfa AESAR Co. All other compounds and solvents were of reagent grade and were used as received. Salen-derivative ligands[32−34] and (hydroxyphenyl)oxazoline[35] were synthesized according to literature methods. Complexes **2**−**7** are stable toward air, moisture, and light.

Spectroscopic analyses were performed on the following instruments: a Shimadzu UV-2505 spectrophotometer, Bruker 200 and 400 MHz NMR spectrometers, and a Perkin-Elmer FTIR Paragon 1000 spectrophotometer. Elemental analyses were performed in duplicates by Desert Analytics, AZ.

Computational Methods. Calculations were carried out using the program Gaussian 94.[36] The geometries and analytical frequencies were calculated at the density functional theory (DFT) level with the Becke3LYP[37] functional. The LanL2DZ basis and effective core potential were used, as well as a quasirelativistic function (ECP) for palladium with a (341/321/31) basis set for the valence electrons[38,39] in conjunction with a 6-31G(d) basis set for all other atoms.

X-ray Structure Analysis for 7. A yellow crystal of **7** was grown by slow diffusion of 1:9 ethyl ether/hexane into a CH_2Cl_2 solution of **7**. A suitable crystal of approximate dimensions $0.1 \times 0.1 \times 0.35$ mm was mounted on a glass fiber. X-ray intensity data were recorded at 298 K on a modified Picker diffractometer with graphite-monochromated Mo Kα radiation. Crystallographic data are summarized in Table 1. Cell parameters were obtained by the least-squares method from the setting angles of 3104 reflections. Three standard reflections were monitored during data collection and showed no significant variation in intensities. Reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out using ψ scans. The structure was solved by Patterson and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at idealized positions and were included in refinement as fixed contributors.

Preparation of 2. In a cold solution, 1.1 g (0.006 mol) of $Pd^{II}Cl_2$ was dissolved in 0.5 mL of concentrated HCl (12 mol L^{-1}) and 30 mL of H_2O. The pH was adjusted to 5−6 with 20% NaOAc. A solution of 1.46 g (0.012 mol) of salicylaldehyde in 20 mL of EtOH was added, and the mixture was stirred for 20 min. The product was filtered off and washed with 25 mL of EtOH and 25 mL of ether. Recrystallization from chloroform yielded 0.66−0.85 g (31−40%) of an orange solid. ^{1}H NMR (CD_2Cl_2): δ 8.31 (s, 1H), 8.23 (s, 1H), 7.45 (m, 4H), 7.03 (d, 1H), 6.96 (d, 1H), 6.69 (t, 2H). IR (cm^{-1}): 1609, 1588, 1427, 1404 (C═C aromatic), 758 (═C−H bend). UV−vis (CH_2Cl_2), λ, nm (ϵ, L mol^{-1} cm^{-1}): 416 (3782), 252 (42 868), 234 sh (28 206).

Method A Exemplified by the Preparation of 3. Equimolar amounts of **2** (1.7 mmol) and ethylenediamine were dissolved separately in chloroform (45 mL). In a round-bottom flask, the solution of ethylenediamine was added to the solution of **2**, and the mixture was refluxed for 20 min and cooled to room temperature. The resulting solution was capped and left overnight. The product was isolated by

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filtration and recrystallized with pyridine to yield 0.79 g (90%) of yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.66 (s, 2H), 7.30 (t, 2H), 7.14 (d, 2H), 6.98 (d, 2H), 6.55 (t, 2H), 3.80 (s, 4H). IR (cm^{-1}): 1633, 1602, 1448 (C═C aromatic), 1191, 1149, 1128 (C═N), 732 (═C−H bend). UV−vis (CH_2Cl_2), λ, nm (ϵ, L mol^{-1} cm^{-1}): 415 (6206), 401 (6044), 241 (43 024). FAB^+/MS: m/z = 372 (M^+ ion; correct isotope for Pd). Anal. Calcd for $C_{16}H_{14}N_2O_2Pd$: C, 51.56; H, 3.79; N, 7.52. Found: C, 51.25; H, 3.79; N, 7.45.

Method B Exemplified by the Preparation of 4. The reaction was performed in flame-dried glassware and under Argon. In a three-neck round-bottom flask, 0.174 g (0.54 mol) of 1,2-*trans*-cyclohexylsalen ligand was dissolved in 20 mL of absolute ethanol. This solution was added via syringe to a solution of 0.131 g (0.5 mol) of $PdCl_2(CH_3CN)_2$ in 20 mL of absolute ethanol. The resulting solution was refluxed for 1 h and then cooled to room temperature. The product was isolated by filtration and washed with ether to yield 0.70 g (70%) of yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.70 (s, 2H), 7.32 (t, 2H), 7.21 (d, 2H), 6.98 (d, 2H), 6.57 (t, 2H), 3.52 (s, 2H), 2.62 (s, 2H), 1.97 (s, 2H), 1.42 (s, 4H). IR (cm^{-1}): 1630, 1600, 1448 (C═C aromatic), 1191, 1152, 1127 (C═N), 747 (═C−H bend). UV−vis (CH_2Cl_2), λ, nm (ϵ, L mol^{-1} cm^{-1}): 413 (5068), 237 (33 304). FAB^+/MS: m/z = 426 (M^+ ion; correct isotope for Pd). Anal. Calcd for $C_{20}H_{20}N_2O_2Pd$: C, 56.28; H, 4.72; N, 6.56. Found: C, 54.80; H, 5.14; N, 7.22.

Preparation of 5. Method A as described for **3** was followed for the synthesis of **5**. Yield: 0.3869 g (55%) of dark brown solid. ^{1}H NMR (CD_2Cl_2): δ 8.57 (s, 2H), 7.69−6.10 (m, 12H). IR (cm^{-1}): 1605, 1458, 1438 (C═C aromatic), 1149 (C═N), 748 (═C−H bend). UV−vis (CH_2Cl_2), λ, nm (ϵ, L mol^{-1} cm^{-1}): 452 (6182), 433 sh (6468), 381 sh (6266), 357 (9898), 314 (13862), 246 (27814). FAB^+/MS: m/z = 420 (M^+ ion; correct isotope for Pd).

Preparation of 6. Method A yielded 0.3966 g (87%) of yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.63 (s, 2H), 7.29 (t, 2H), 7.16 (d, 2H), 6.98 (d, 2H), 6.56 (t, 2H), 3.72 (t, 4H), 2.08 (m, 2H). IR (cm^{-1}): 1616, 1540, 1474, 1452 (C═C aromatic), 1128 (C−N stretch), 742, 726 (═C−H bend). UV−vis (CH_2Cl_2), λ, nm (ϵ, L mol^{-1} cm^{-1}): 395 (5354), 313 sh (5664), 242 (43 138). FAB^+/MS: m/z = 386 (M^+ ion; correct isotope for Pd).

Preparation of 7. In a three-neck round-bottom flask, 0.204 g (0.78 mmol) of $PdCl_2(CH_3CN)_2$ was dissolved in 20 mL of CH_2Cl_2 by gentle heating. At room temperature, 0.167 g (1.02 mmol) of the ligand 2-(2′-hydroxyphenyl)-2-oxazoline dissolved in 20 mL of CH_2Cl_2 was added in one portion, and the reaction solution was stirred under argon for 40 min. The progress of the reaction was followed by TLC. The orange solution was filtered, and the filtrate was concentrated under vacuum to afford 0.082 g (37% yield) of a yellow solid, which was recrystallized from CH_2Cl_2. ^{1}H NMR (CD_2Cl_2): δ 7.57 (d, 2H), 7.20 (t, 2H), 6.84 (d, 2H), 6.54 (t, 2H), 4.60 (t, 4H), 4.14 (t, 4H). FAB^+/MS: m/z = 430 (M^+ ion; correct isotope pattern for Pd).

General Catalytic Procedure for Cyclopropanation. A round-bottom flask was charged with complex **2** (0.01 mmol) and the appropriate olefin (1.00 mmol) in 5 mL of $CDCl_3$ at room temperature. Ethyl diazoacetate (2.0 mmol) in 1 mL of $CDCl_3$ was added via a pump syringe over 1 h, and the reaction mixture was allowed to stir for 24 h prior to NMR and GC analyses.

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Supporting Information Available: Figures showing a 2D NMR spectrum of complex **2** in DMSO and calculated structures and relative energies for the stereoisomers of bis(salicylaldehydato)palladium(II), **2**, and tables of structure refinement details, atomic coordinates, thermal parameters, bond distances, and bond angles for complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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